COMPARISON OF ASTM D613 AND ASTM D6890

FINAL REPORT
TFLRF No. FR 467

by
George R. Wilson, III

U.S. Army TARDEC Fuels and Lubricants Research Facility
Southwest Research Institute® (SwRI®)
San Antonio, TX

for

Patsy A. Muzzell
U.S. Army TARDEC
Force Projection Technologies
Warren, Michigan

Contract No. W56HZV-09-C-0100 (WD001)

April 2016

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14. ABSTRACT

This program evaluated the comparative results between ASTM D613 Cetane Number testing an ASTM D6890 Derived Cetane Number testing. Particular emphasis was placed on evaluating fuels, and blends thereof, having cetane values outside of the normal range of the methods, both high and low. The Derived Cetane Number was found to be suitable for routine use in determining the cetane value of distillate hydrocarbons.

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EXECUTIVE SUMMARY

The U.S. Army needs to understand how well the ASTM D6890 Derived Cetane Number (DCN) test correlates to ASTM D613 Cetane Number (CN) test for a variety of fuels. This interest covers both petroleum-based and synthetic-based, as well as blends thereof in order to improve the confidence in using DCN as a replacement test for CN.

The basic test program was to perform CN and DCN analysis on a series of eighteen (18) test fuels. The testing consisted of running one (1) ASTM D613 CN test and three (3) ASTM D6890 DCN tests on each fuel. The test fuels consisted of six (6) neat fuels, consisting of two (2) refined fuels and four (4) synthetic fuel blending materials, and twelve (12) blends thereof. The DCN testing was done in random order to enhance the understanding of how the equipment would perform in typical operations.

This testing resulted in the following observations:

- ASTM D613 CN testing, as routinely run, cannot measure the range of synthetic materials that have been used to make alternative fuels.
- ASTM D6890 DCN testing performs well within the precision stated in the method even with materials outside of the stated scope.
- The correlation between CN and DCN is very good although the expected cross method reproducibility limits are exceeded for some blends made with ATJ SPK.
- The volumetric additive properties of CN were used for blending work for DCN values too.

This test program supports the proposition that DCN testing, by ASTM D6890, is satisfactory for evaluating the cetane values for hydrocarbons fuels and fuel blends, even for components out of scope of the device. That is important for U.S. Army interests in considering the commitment by the U.S. DOD to the use of alternative fuels and fuel components. Since some of these components have cetane values outside of the routine range of traditional CN testing by ASTM D613, this is an important advantage in fuel blending and disposition. Based on this analysis, DCN by ASTM D6890 should become the preferred method for determining the cetane value for the U.S. Army.

FOREWORD/ACKNOWLEDGMENTS

The U.S. Army TARDEC Fuel and Lubricants Research Facility (TFLRF) located at Southwest Research Institute (SwRI), San Antonio, Texas, performed this work during the April 2015 through October 2015 under Contract No. W56HZV-09-C-0100. The U.S. Army Tank Automotive RD&E Center, Force Projection Technologies, Warren, Michigan administered the project. Mr. Eric Sattler (RDTA-SIE-ES-FPT) served as the TARDEC contracting officer's technical representative. Patsy A. Muzzell of TARDEC served as project technical monitor.

The author would like to acknowledge the contribution of the TFLRF technical support staff along with the administrative and report-processing support provided by the TFLRF administrative staff.

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ACRONYMS AND ABBREVIATIONS

1-D	Special-Purpose, Light Middle Distillate Fuel
2-D	General Purpose, Middle Distillate Fuel
AIT	Autoignition Temperature
ATDC	After Top Dead Center
ATJ	Alcohol to Jet
CI	Compression Ignition
CN	Cetane Number
CN_{ARV}	Cetane number accepted reference values
CONUS	Continental United States
DCN	Derived Cetane Number
FT	Fischer Tropsch
HEFA	Hydroprocessed Esters and Fatty Acids
HMN	Heptamethylnonane
HRD	Hydrotreated Renewable Diesel
ID	Ignition Delay
IQT	Diesel Fuel Ignition Quality Tester
IR	Intermediate Reproducibility
PQAS-E	Petroleum Quality Analysis System-Enhanced
r	Repeatability
R	Reproducibility
SPK	Synthetic Paraffinic Kerosene
SwRI	Southwest Research Institute
ULSD	Ultra Low Sulfur Diesel

1.0 INTRODUCTION

This report compares the use of the ASTM D6890 method for generating the Derived Cetane Number (DCN) to the traditional ASTM D613 method for generating the Cetane Number (CN). In particular there is an emphasis on understanding how these industry standard methods work when using synthetic fuels and blends using synthetic fuel components. The report covers the following major topics:

1. Cetane Value Testing – This section includes a short discussion on the nature of diesel ignition. Following that discussion is a review of the nature and origin of the Cetane Number Scale.
2. Test Program – This section covers the three major components of the test program
    a. The test methods used to evaluate the cetane value
    b. The fuels, neat and blended, used as test material
    c. The testing to be conducted on the fuel samples
3. Program Evaluation – This section reviews the data generated as follows
    a. A review of the data generated and a discussion on any issues affecting the testing or the results
    b. An analysis of the precision of these data in relation to understood precision of the test
    c. A review of how well the two methods correlate with this particular set of samples
    d. A discussion of how DCN data may be used effectively

In conclusion there is a review of program in context of the samples used. This covers how the program has successfully shown that DCN testing by ASTM D6890 is suitable for use in research and specifications associated with cetane value testing.

2.0 CETANE VALUE TESTING

2.1 COMPRESSION IGNITION QUALITY OF DISTILLATE FUELS

Diesel engines, as generally understood, are diesel cycle internal combustion engines which rely on compression ignition (CI) for motive power. Compressing a gas elevates its temperature. When a fuel is introduced into a compressing air mixture, it will autoignite [1] when sufficient temperature and pressure levels are reached. The point at which this will happen is a function of the autoignition temperature (AIT) of the fuel.

Table 1. AIT and CN for Selected Diesel Range Hydrocarbons [2]

Compound	Carbon No.	Cetane No.	Autoignition Temp, °C
n-Hexadecane	C16	100	202
1-Hexadecane	C16	84	240
Heptamethylnonane	C16	15	472
n-Nonylbenzene	C16	50	n/a
n-Dodecane	C12	88	204
3-Ethyldecane	C12	55	n/a
Dicyclohexyl	C12	47	245
Pentamethylheptane	C12	10	n/a
1-Methylnaphthalene	C11	0	529
n-Decane	C10	77	208
sec-Butylbenzene	C10	6	415
Decalin	C10	42	250

The AITs noted in Table 1 cover a wide range of temperatures. In particular, note the variations for chemicals with the same carbon number (Cxx). They give a general idea of the ignition quality but are not accurate in practice. The AIT test [2] is a static test that relies simply on heating a test fluid gradually in the presence of air until the vapors ignite. A CI engine is a dynamic system wherein other fuel properties, such as viscosity, vapor pressure, chemical structure, etc., have an effect on how the fuel works. Knowing that these additional items impact CI quality of a fuel does not easily translate into a formula for evaluation of CI quality.

2.2 UNDERSTANDING THE CETANE NUMBER SCALE

The approach taken to providing a relative evaluation of CI ignition quality was to develop a ratiometric scale based on comparing a candidate fuel to blends of known ignition quality blended from standard reference fuels. The resulting value is known as the Cetane Number (CN). The standard reference chemicals are illustrated in Figure 1:

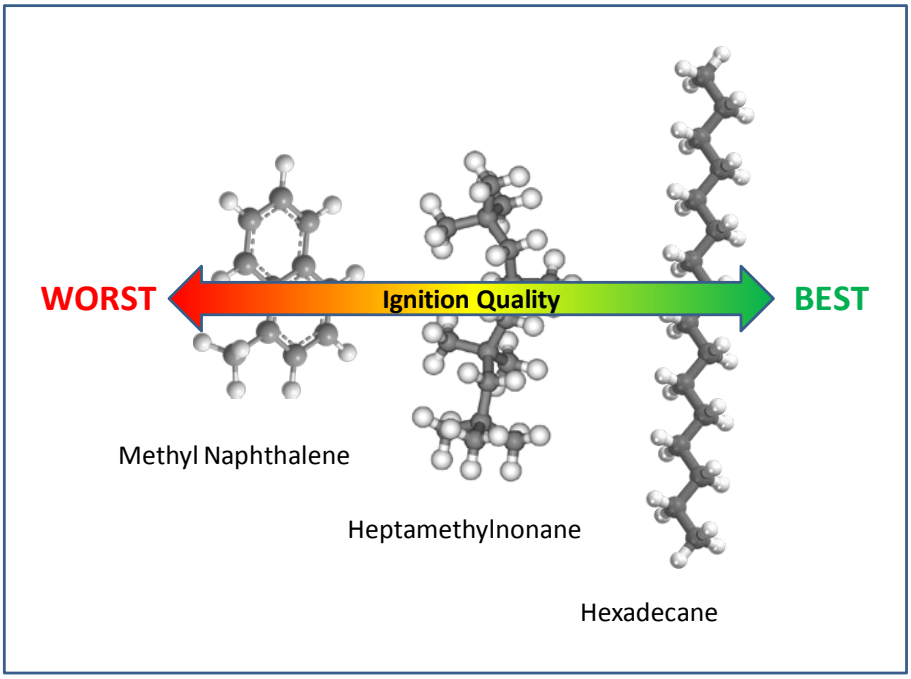

Figure 1. Ignition Quality Compared to Structure

The best ignition quality comes with normal paraffins. Branching reduces the ignition quality. Aromatics have poor ignition quality at best (but offer energy density). In the program that developed the CN test, the initial reference fuels chosen were methylnaphthalene, CN = 0, and *n*-hexadecane (*n*-cetane), CN = 100. With experience, methylnaphthalene proved to be an impractical material for reference values. The ASTM Diesel National Exchange Group ran a study and determined that heptamethylnonane (HMN), CN = 15, was an appropriate substitute. Reference fuel CN values, known as accepted reference values (CN_{ARV}) are determined from the ratiometric value of the mixture of hexadecane and heptamethylnonane, calculated as follows:

$$CN_{ARV} = volume\ \%\ n\text{-}cetane + 0.15(volume\ \%\ HMN)$$

Table 1 shows the CN values for a series of chemicals in the diesel fuel range. Examining this data will show how structure effects CN. For instance, compare the three C16 paraffins. The straight normal paraffin, n-cetane, has a value of CN = 100. A single branching methyl reduces the value to CN = 88. Maximizing the branching with HMN, having five methyls on a seven carbon backbone, and the value becomes CN = 15. It is worth noting that this is a relative scale based on these reference materials. There are chemicals that have worse ignition quality, CN < 0, and better ignition quality, CN > 100.

As stated previously, the AIT gives a general idea of the ignition quality of fuels but it is not accurate. That poor relationship can be inferred from the data in Table 1 but a comparative plot provides a better picture. The following graph (Figure 2) includes all the data from the source used for Table 1.

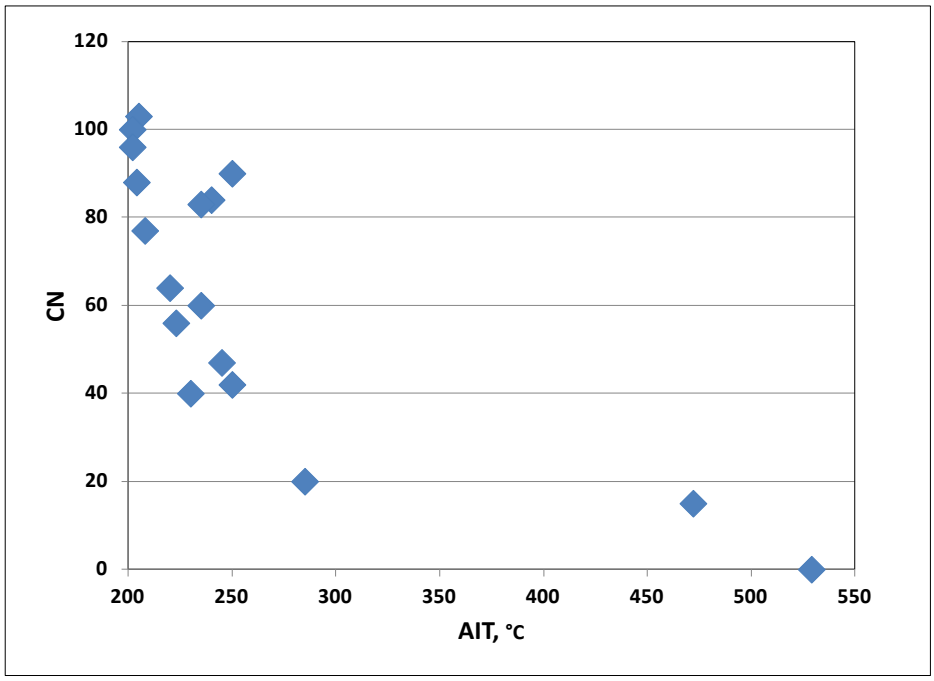

Figure 2. Cetane Number vs. Autoignition Temperature

If all of the potential chemicals used in fuel had the key properties associated with ignition quality documented, it might be possible to calculate the ignition quality (if you could determine the chemical makeup of the fuel). This is simply not possible, in practice, so the use of tests that

generate data compared to reference values is more practical. The tests used to determine cetane value directly use some form of a laboratory practical combustion chamber.

There are methods available to estimate the CN as a function of the physical chemical properties of diesel fuels based on a statistical analysis of hundreds of fuels. These estimates are referred to by the term Cetane Index and they work fairly well for refined fuel but they are not suitable [3] for evaluating synthetic or semi-synthetic fuels whose compositions vary significantly from the refined statistical norms. Thus, this program focuses exclusively on methods that measure CI ignition quality directly.

3.0 TESTING PROGRAM

This section of the report discusses the methods used, the fuels selected and blended, and testing conducted.

3.1 CETANE TEST METHODS

The following test laboratory combustion test methods were used in this program:

3.1.1 Cetane Number by ASTM D613 [4] -

This is the traditional method for evaluating the ignition quality of distillate fuels. Practically, it is a variable volume combustion chamber where the compression ratio is adjusted to give a standard ignition delay (ID) of 13° After Top Dead Center (ATDC). The compression ratio of a test fuel is compared to the compression ratios of blends of known cetane reference fuels. This value is measured in a large scale test device known as a Cetane Engine (Figure 3).

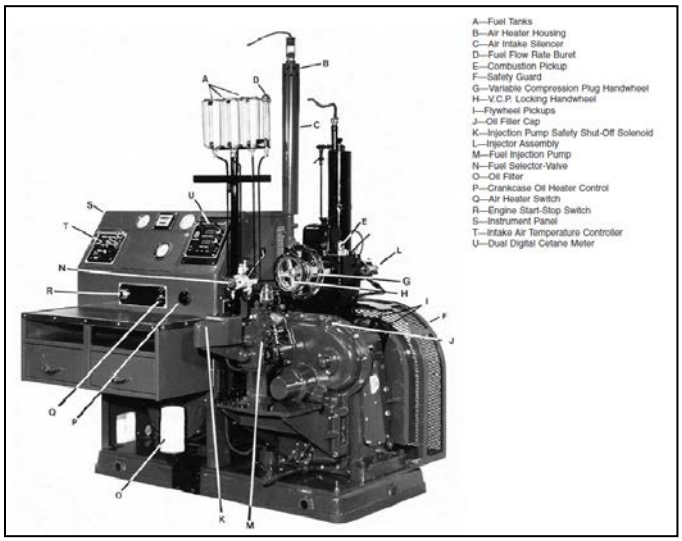

Figure 3. Cetane Engine

3.1.2 Ignition Delay and Derived Cetane Number by ASTM D6890 [5] -

This is the more modern approach to evaluating the ignition quality of distillate fuels. It is a fixed combustion chamber where the ID is measured. The DCN is calculated by applying a correlation equation to the measured ID. The method is embodied in a device called the Diesel Fuel Ignition Quality Tester (IQT) as shown in Figure 4.

Figure 4. Diesel Fuel Ignition Quality Tester (IQT)

The Cetane Index methods, ASTM D976 or ASTM D4737, were not used in this program. Although they are used as a report item in the JP-8 specification [6], they are not accurate with semi-synthetic fuel components, neat or blended.

3.2 TEST FUELS

This test program was conducted with eighteen (18) test samples. These samples consisted of six (6) neat fuels and twelve (12) blends thereof. The six neat fuels covered a range of cetane values in excess of the normal fuel experience for conventional (petroleum) diesel fuels. This is important because many proposed alternative fuels have ignition qualities well outside the range normally associated with refined diesel fuel, 30 CN to 65 CN.

3.2.1 Neat Fuels Used In The Program

1) DF2 – Standard refined 2-D S15 [7] ULSD diesel fuel. This is standard commercial diesel fuel that is sometimes used by the U.S. Army in CONUS.
2) JP-8 – Standard refined military jet fuel. This is the standard tactical and expeditionary fuel used by the U.S. Army under the Single Fuel Forward doctrine.
3) HRD – Hydroprocessed Renewable Diesel, aka Green Diesel. This fuel is derived from organic fats and oils. The fats and oils are hydrotreated to remove oxygen and mildly isomerized to provide the needed low temperature flow. This material typically has superior cetane value properties.
4) FT SPK – Fischer-Tropsch Synthetic Paraffinic Kerosene. This is material made in accordance with Annex A1 of ASTM D7566 [8]. This fuel is from a Fischer-Tropsch plant that produces paraffin wax which is subsequently hydrocracked and isomerized to produce jet fuel range material with excellent low temperature properties. This version of FT SPK has very good cetane value properties [9].
5) HEFA SPK – Hydroprocessed Esters and Fatty Acid Synthetic Paraffinic Kerosene. This material is made in accordance with Annex A2 of ASTM D7566. This is an extension of the HRD process wherein the paraffin wax material, generated from hydrotreating esters

and fatty oils, is then hydrocracked and isomerized to produce jet fuel range material with excellent low temperature properties and good cetane value properties.

6) ATJ SPK – Alcohol to Jet Synthetic Paraffinic Kerosene. This material is generated by the sequential alkylation of isobutene derived from isobutanol. It is approximately 80% C12, pentamethylheptane, and 20% C16, heptamethylnonane. As could be predicted from the data in Table 1, this material has a very poor cetane value. The ATJ SPK blendstock is currently under review for inclusion into ASTM D7566 (where it will likely be Annex A5).

3.2.2 Fuel Blends Used In The Program

The following twelve (12) blends were made for this program. Each listing (x:x y/y) shows the blend ratio (x:x) and the components used (y/y) respectively.

1) 1:1 JP-8 / FT SPK
2) 1:1 JP-8 / HEFA SPK
3) 1:2 JP-8 / FT SPK
4) 1:2 JP-8 / HEFA SPK
5) 3:1 JP-8 / ATJ SPK
6) 3:1 DF-2 / ATJ SPK
7) 1:1 DF-2 / FT SPK
8) 1:1 HRD / ATJ SPK
9) 1:1 DF-2 / ATJ SPK
10) 1:3 JP-8 / ATJ SPK
11) 1:1 HRD / FT SPK
12) 3:3:1 JP-8 / HEFA / ATJ

3.3 TEST PROGRAM

Each of the eighteen (18) samples, six (6) neat and twelve (12) blended, were tested as follows:

1) One (1) test each by ASTM D613 Cetane Engine to provide a Cetane Number (CN) for each sample
2) Three (3) tests each by ASTM D6890 IQT, providing the following data for each sample:
    a. Derived Cetane Number (DCN)
    b. Ignition Delay (ID)

To maximize the value for the IQT testing, the test samples were randomized. Fifty four (54) individual samples were prepared and then that list of samples was reordered using a random order technique in a spreadsheet. The samples were then tested in that order. This provided a more normal assessment of how well a single lab might reproduce data.

4.0 EVALUATION

4.1 THE RESULTS FROM THE ASTM D613 AND ASTM D6890 TESTING

The results from the testing described in 3.3 above are shown in Table 2. The data is reported in the format established by the respective test methods, rounded to the nearest 0.1 for cetane values (CN and DCN) and the nearest 0.01 for ID. The DCN is calculated from the ID thus the referenced replicates are the same test for each sample (DCN Replicate 1 = ID Replicate 1).

Table 2. Test Results

			D613	D6890 Derived Cetane No.			D6890 Ignition Delay		
Test Samples		**Sample ID**	**Cetane No.**	**Replicate 1**	**Replicate 2**	**Replicate 3**	**Replicate 1**	**Replicate 2**	**Replicate 3**
Blend Stocks									
CT01	DF2	CL15-7891	48.8	46.1	45.1	46.0	4.49	4.60	4.50
CT02	JP-8	CL15-7872	48.6	47.4	48.1	47.6	4.34	4.27	4.33
CT03	HRD	CL15-7890	> 74.8	76.5	76.0	75.6	2.75	2.76	2.78
CT04	FT SPK	CL15-7888	60.2	57.7	57.8	57.9	3.51	3.50	3.49
CT05	HEFA SPK	CL15-7889	55.4	58.2	58.0	58.5	3.47	3.48	3.49
CT06	ATJ SPK	CL15-7873	< 21.4	16.0	15.7	16.4	19.81	20.40	18.90
Fuel Blends									
CB01	1:1 JP-8 / FT SPK	CL15-7892	54.3	52.3	52.3	51.9	3.90	3.90	3.94
CB02	1:1 JP-8 / HEFA SPK	CL15-7893	50.4	52.3	52.6	52.3	3.91	3.88	3.90
CB03	1:2 JP-8 / FT SPK	CL15-7897	52.6	54.6	54.0	54.2	3.72	3.77	3.76
CB04	1:2 JP-8 / HEFA SPK	CL15-7899	52.7	54.6	54.3	54.3	3.72	3.74	3.74
CB05	3:1 JP-8 / ATJ SPK	CL15-7874	41.7	42.5	42.8	42.5	4.91	4.86	4.91
CB06	3:1 DF-2 / ATJ SPK	CL15-7900	42.3	41.3	40.8	41.7	5.07	5.14	5.01
CB07	1:1 DF-2 / FT SPK	CL15-7918	50.2	52.7	51.7	52.3	3.87	3.95	3.90
CB08	1:1 HRD / ATJ SPK	CL15-7919	46.0	51.6	51.4	51.6	3.96	3.97	3.96
CB09	1:1 DF-2 / ATJ SPK	CL15-7920	32.8	35.6	34.8	36.3	6.00	6.16	5.87
CB10	1:3 JP-8 / ATJ SPK	CL15-7875	25.0	28.4	28.4	28.6	7.87	7.87	7.79
CB11	1:1 HRD / FT SPK	CL15-7921	65.0	67.2	66.7	68.8	3.04	3.06	2.98
CB12	3:3:1 JP-8 / HEFA / ATJ	CL15-7922	48.5	49.4	49.6	49.8	4.15	4.14	4.12

Notes on the test results:

1) ASTM D613 Testing – Two samples, HRD and ATJ SPK, do not have actual values reported. The reported results, HRD > 74.2 CN and ATJ SPK < 21.4 CN, reflect standard practice for cetane engine testing [10]. The standard reference fuels are typically only used in calibrating new or repaired equipment. Routine operations rely on secondary reference fuels described in section 8.4 of ASTM D613 as follows:

   a. *T Fuel* – Diesel fuel with a CN_{ARV} typically in the range of 73 to 75

   b. *U Fuel* – Diesel fuel with a CN_{ARV} typically in the range of 20 to 22

   The values quoted in Table 2 for HRD and ATJ SPK reflect the values for *T Fuel* (CN = 74.8) and *U Fuel* (CN = 21.4) in use at SwRI at the time of the testing.

2) ASTM D6890 Testing – The IQT calculates the DCN from the ID. The standard calculation is found in section 13, Calculation, of ASTM D6890. It is:

$$DCN = 4.460 + 186.6/ID$$

This calculation, however, is only good for the ID range of 3.1 ms to 6.5 ms. This program has four samples, two neat and two blends, with ID results outside of that range. For those samples, the calculation (from D6890 Annex X2) is:

$$DCN = 83.99(ID - 1.512)^{(-0.658)} + 3.547$$

The standard report from the IQT does not identify the equation being used but it was checked as part of the program and it was determined that the instrument switches the calculation as appropriate for ID measured.

4.2 ESTIMATED INTERMEDIATE PRECISION OF ASTM D6890 BASED ON THIS TEST PROGRAM [11]

As noted in section 3.3 above, the IQT samples were prepared individually (three (3) separate samples for each test fuel) and those samples were then randomized before testing. This approach was used to provide a better understanding of how the IQT works in practice, where repeated attempts on the same sample are unlikely during routine testing. This places the testing conducted between the concepts of repeatability (r), where time, place, operator, etc. are the same, and reproducibility (R), where time, place, operator, etc. are different. The approach used in this testing is classified [12] as having *intermediate precision conditions* and they result in *intermediate precision*. In this program the precision estimate is called intermediate reproducibility (IR).

Precision describes how well results agree. Precision analysis is used to provide an expectation of the quality of the data. In this program the estimated IR is compared to the precision stated in the method. To make this estimate, the first step was to determine a standard deviation, σ, for the triplicate samples. That value is then used to calculate the IR using the following formula:

$$IR = 2.8\sigma$$

This was calculated for both DCN, IR_{DCN}, and ID, IR_{ID}, for each fuel sample. The formula is the standard calculation for determining the 95% confidence level in standard precision program. It means that, on average, the difference between any two tests will not exceed the calculated value

more than one time in twenty. The precision statements in most methods resolve the numbers for individual samples into a statement that covers the range in question, which is, in effect, an average of 95% confidence levels.

So by this understanding, the precision information illustrated in Figure 5 and Figure 6 shows how well the IQT device performed the ID and DCN analysis in this program. Does that also inform on the correctness of the data in relation to the CN? No, that would be considered a question of accuracy. That would require the use of standards with acceptable reference values, ARV, for CN, which ASTM D6890 does not use. The question of how well this method reproduces CN values will be covered in section 4.3, Correlation of ASTM D6890 with ASTM D613.

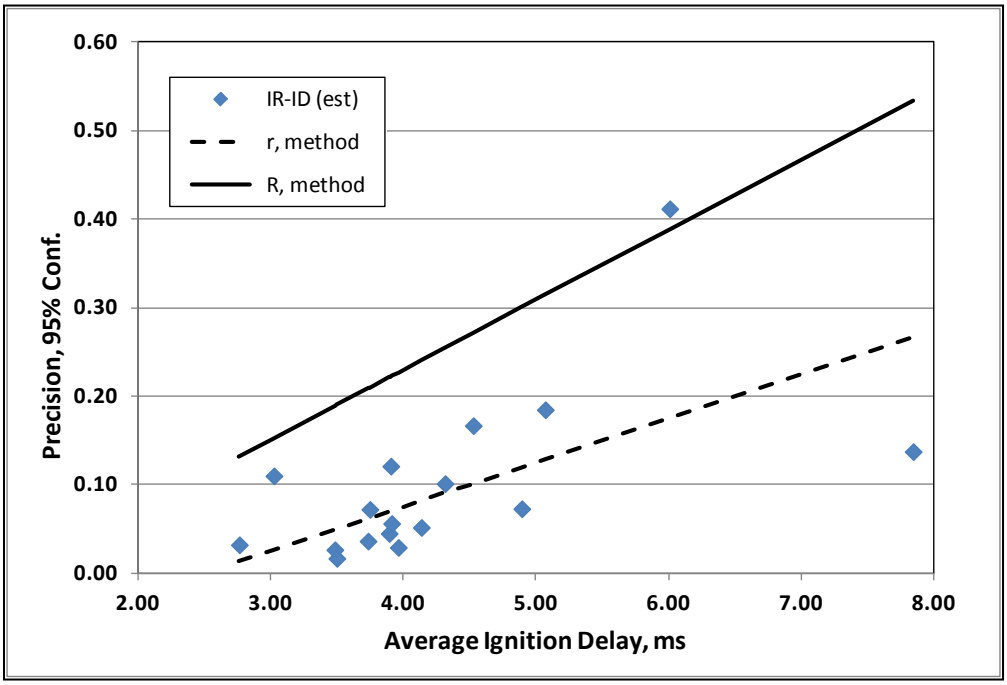

Figure 5. Ignition Delay Precision

The graph in Figure 5 does not include the ID information for ATJ SPK. The precision statement only covers the range of 3.1 ms to 6.5 ms and while one can reasonably expand to cover most of the samples, the 19.71 ms for ATJ SPK is too far out to be of value in evaluating the system

performance. Conversely, the corresponding DCN value for ATJ SPK, 16.0 DCN, is included in Figure 6 as it fits well into expectations even though it is not in the scope of the method either.

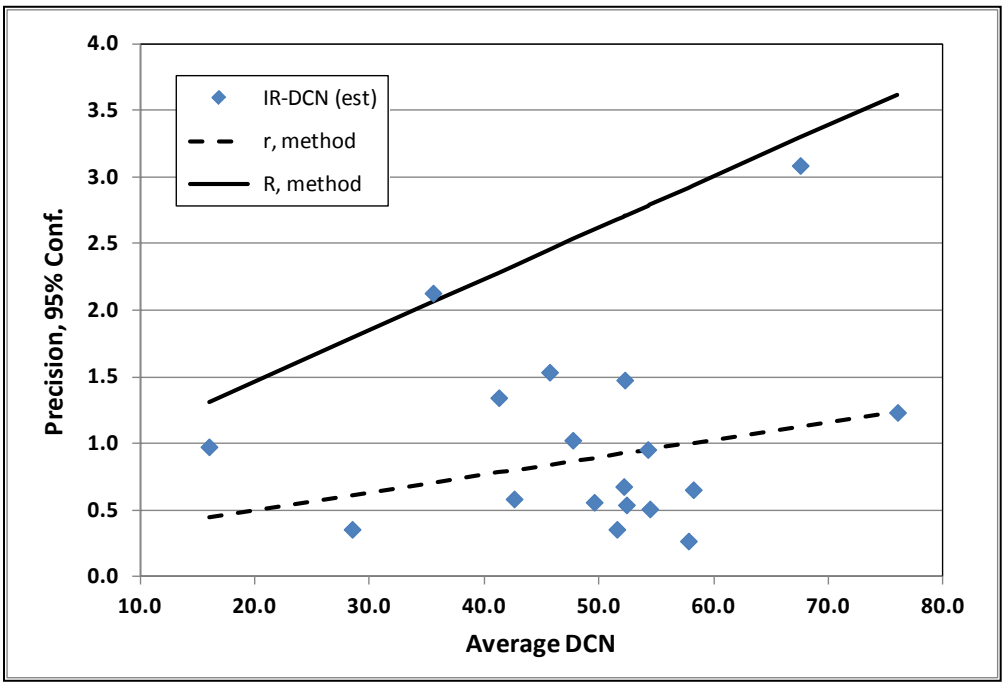

Figure 6. Derived Cetane Number Precision

Overall the results are very good. If trend lines are projected through the estimated IR_{ID} and IR_{DCN} data for the program, they look very similar to the illustrated repeatability, r, limits. (This is not done because there is insufficient data to establish a comparable precision value.) The grouping around the repeatability function line, with some better and some worse, is expected as the test conditions are very close to those needed to establish repeatability.

4.3 CORRELATION OF ASTM D6890 WITH ASTM D613

Figure 7 illustrates comparative data for sixteen (16) of the test fuels in this program. As noted in section 4.1 above, for two samples, HRD and ATJ SPK, the CNs could not be resolved using industry standard practice. These are also fuels components well outside of the expected norms for cetane value.

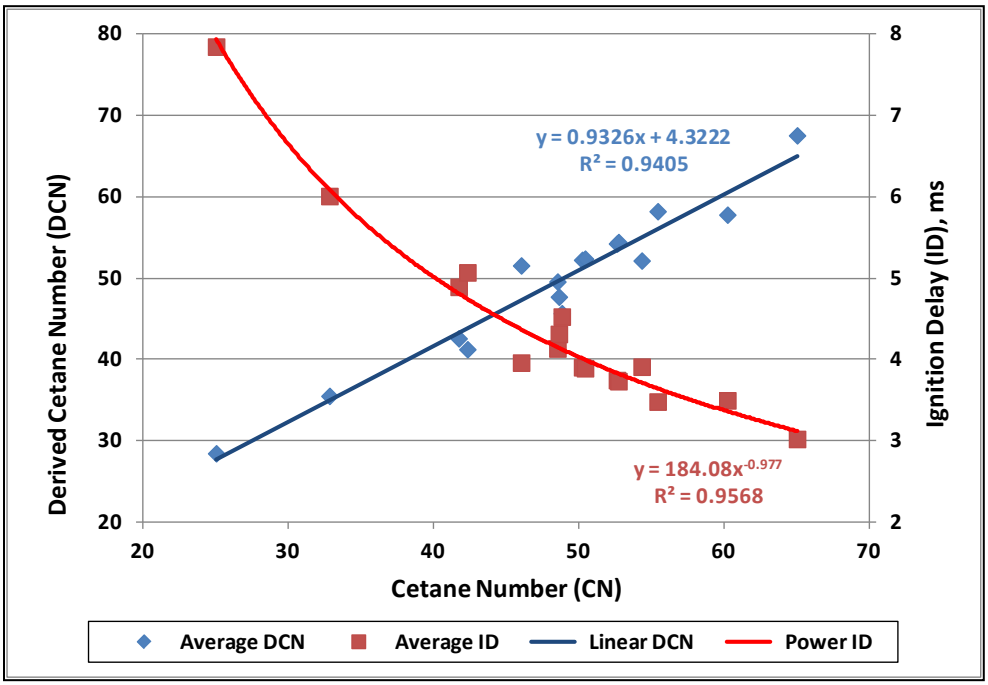

Figure 7. Correlation of ASTM D6890 with ASTM D613

As might be expected, for a test intended to correlate with ASTM D613, the correlation of the IQT data with the cetane engine data is excellent. The correlation coefficient for ID, R_{ID} = 0.9782, is slightly better than that for DCN, R_{DCN} = 0.9698. This could be due to a couple of reasons. First, DCN is derived from ID so there can be some degradation in the conversion. Second, the DCN values were derived from two equations, as noted in section 4.1 above. (R^2, as commonly used in graphing applications, is the Coefficient of Determination).

The statistical relationship between ID and CN, as illustrated in Figure 7, is a power series. This is a very similar relationship as seen between cetane and AIT in Figure 2. This is reasonable as ASTM D6890 is really an alternative approach to measuring autoignition, run under different conditions designed to be more similar to those found in a CI engine. The fundamental impact of molecular structure remains the same.

The relationship between DCN and CN is, as expected, linear. It is not, however, a unity (DCN = CN) relationship. The data does involve two separate DCN calculations, as noted in

section 4.1 above, but even if that were not the case, this would not be unusual. The primary DCN correlation was established from many more combinations of ID and CN than in this program. Any small subgroup of CN to DCN comparisons will generally have a nonunity correlation.

As part of development of ASTM D6890, the methods technique for generating a DCN was compared formally to the CN generated by ASTM D613 using ASTM D6708 [13]. This effort generates information on intermethod precision, Rxy. For ASTM D6890, this resulted in the following formula:

$$Rxy = 0.1094 \times [(DCN + CN_{D613})/2 - 11.02]$$

As an additional check on how well these methods correlate, this formula was applied to the data from the fuels for which both CN and DCN values were available. The results of this analysis are shown in Figure 8.

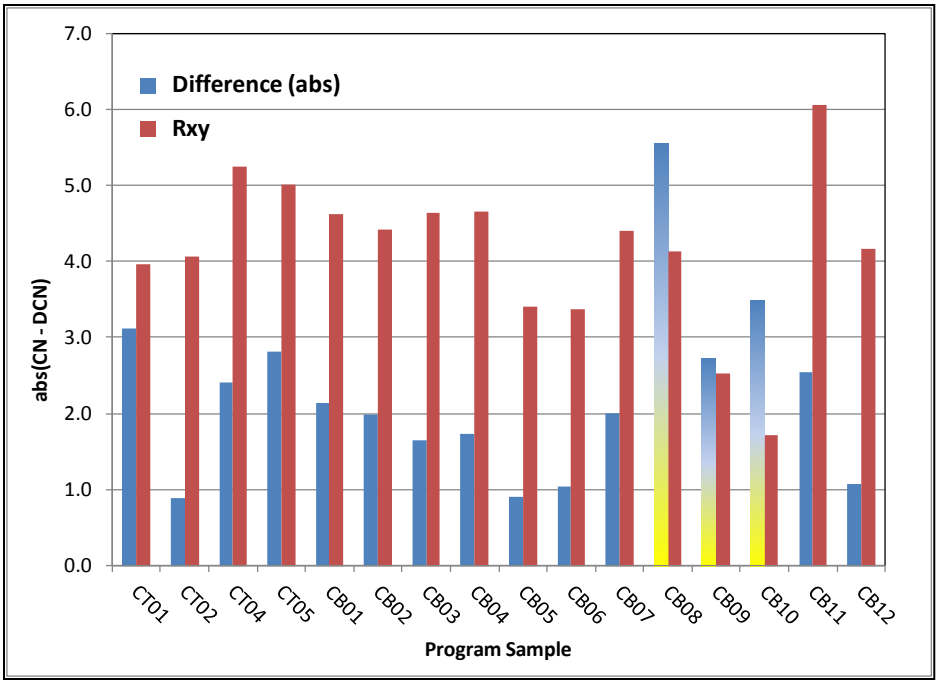

Figure 8. Intermethod Precision, Rxy, Analysis

In Figure 8 the absolute difference between results, abs(CN-DCN), is plotted next to the calculated intermethod precision, Rxy. Intermethod precision, like other precision estimates, describes a 95% confidence limit, where no more than one in twenty should exceed the calculated limit. In this testing three of sixteen, 19%, of the pairs exceed the expected difference.

Consider, however, that the three samples that do exceed the calculated Rxy, CB08-10, are all blends (see Table 2) with a very high percentage, 50-75%, of ATJ SPK. This is consistent with previous testing [14] conducted at TFLRF that showed high percentages of ATJ SPK resulted in a significant deviation between ASTM D613 and ASTM D6890 results. The ATJ SPK has an ID, 19.71 ms, so far outside the scope of the method, 3.1 ms to 6.5 ms, that information therefrom has no precision validity. That can be extended to the understanding that because materials with that long of an ID are not in the scope, then the unique chemical characteristics of those materials are not accounted for either. While the DCN of the three mixtures is within the scope of the method, high percentages of the high ID material may affect the performance in the IQT system.

4.4 USING ASTM D6890 DATA

The diesel fuel specification, D975, allows the use of DCN data for all 1-D and 2-D grades of diesel fuel (ASTM D613 is the referee). 1-D diesel fuel is similar to aviation turbine fuel. Although the physical properties do not completely overlap, it is understood that it works with the same cetane value scale. The JP-8 specification requires DCN testing for semi-synthetic blends made with FT SPK or HEFA SPK.

Method ASTM D613 is replete with the idea that the CN is suitable for simple arithmetic. That is the blend CN is sum of the fractional cetane numbers of the blend components based on volume, thus:

$$CN_{Total} = (vol\,\% \times CN_a) + (vol\,\% \times CN_b) + \cdots + (vol\,\% \times CN_n)$$

Method ASTM D6890 does not highlight this as it is primarily a method to determine the ID with the cetane value being derived therefrom. However, the DCN should be the arithmetic equivalent to CN. This concept was applied to the data for the twelve (12) blends from this

program. The average DCN values for the neat fuels used for making the blends were used to predict a DCN for the finished blend. That calculated DCN was then compared to the actual measured DCN. For simple comparative purposes, the same effort was made for ID. The calculated results are shown in Table 3.

Table 3. Calculated Derived Cetane Number and Ignition Delay

Fuel Blends	Comp #1	Comp #2	Comp #3	Est DCN	Comp #1	Comp #2	Comp #3	Est Delay
1:1 JP-8 / FT SPK	47.7	57.8		52.8	4.31	3.50		3.91
1:1 JP-8 / HEFA SPK	47.7	58.2		53.0	4.31	3.48		3.90
1:2 JP-8 / FT SPK	47.7	57.8		54.4	4.31	3.50		3.77
1:2 JP-8 / HEFA SPK	47.7	58.2		54.7	4.31	3.48		3.76
3:1 JP-8 / ATJ SPK	47.7	16.0		39.8	4.31	19.71		8.16
3:1 DF-2 / ATJ SPK	45.7	16.0		38.3	4.53	19.71		8.32
1:1 DF-2 / FT SPK	45.7	57.8		51.7	4.53	3.50		4.01
1:1 HRD / ATJ SPK	76.0	16.0		46.0	2.76	19.71		11.23
1:1 DF-2 / ATJ SPK	45.7	16.0		30.8	4.53	19.71		12.12
1:3 JP-8 / ATJ SPK	47.7	16.0		23.9	4.31	19.71		15.86
1:1 HRD / FT SPK	76.0	57.8		66.9	2.76	3.50		3.13
3:3:1 JP-8 / HEFA / ATJ	47.7	58.2	16.0	47.7	4.31	3.48	19.71	6.16

The data generated appears intuitively right, even for the ID, as one would expect a material with a very poor ignition quality to have a very adverse effect on blend. Plotting the calculated data, as seen in Figure 9, shows the reality of the effort.

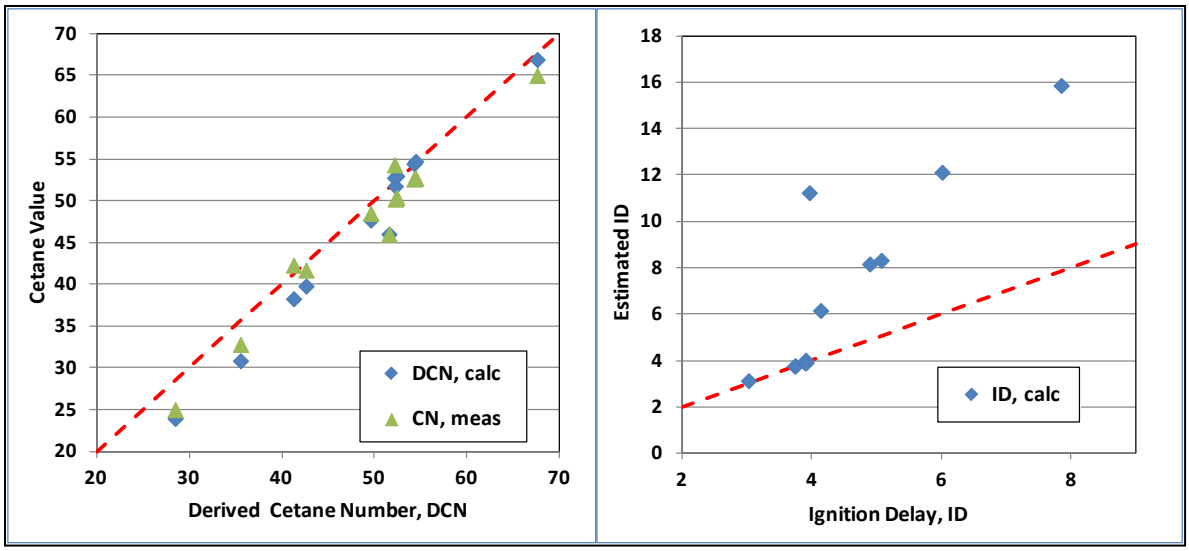

Figure 9. Derived Cetane Number and Ignition Delay, Calculated vs. Measured

In Figure 9 the dashed red lines represent unity, calculated value = measured value, and is used for reference. The calculations using DCN values show that the same additive principle works fairly well for DCN as it does for CN. For reference, the actual CNs for the blends are also plotted. For several data points, the calculated DCN proved better at predicting the CN than did actually running the test. This is probably an artifact of the unusual blend materials used in this program.

The calculations using ID values work very poorly. Since ID is a power function, this is to be expected. There is some belief that ID is a superior method for describing combustion performance compared to CN. That may be true but it is not useful for fuel blending. It would require transformation to a linear function, like the DCN, to be useful. It is possible that an alternative linearizing function, divorced from correlating with the CN, could provide a more accurate value for blending.

Any use of ID in anything besides research should be considered carefully. There are three ID tests that generate DCN values approved for use with the ASTM D975 specification. The other tests are ASTM D7170 [15] and ASTM D7668 [16]. They both use a different approach to generate autoignition and produces different ID values for the same DCN. ASTM D6890 and ASTM D7170 are compared in Figure 10.

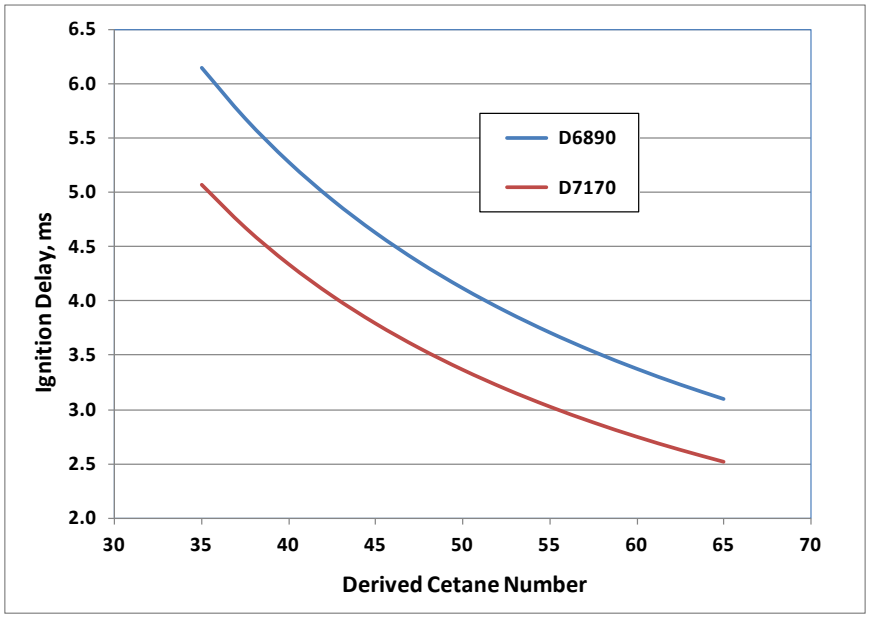

Figure 10. Data Range, ASTM D6890 vs. ASTM D7170

An ID of 4.0 ms would mean a DCN of 51.1 for ASTM D6890 and a DCN of 42.9 for ASTM D7170. ASTM D7668 uses an additional factor, combustion delay, so it cannot be compared by ID. Conversely, a cetane value of 40 would be equivalent, within the cross method precision, for ASTM D613 CN, ASTM D6890 DCN, ASTM D7170 DCN and ASTM D7668 DCN. Any use of ID in research or programs would have to clearly identify the technique being used.

5.0 SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 SUMMARY

Following are the highlights of this program

- In Section 2.0, the basic concept of cetane value was shown to be related to autoignition properties of distillate fuels. This concept was then associated with the need for practical means of evaluating that property in a system too complex for direct calculation.
- In Section 3.0 the test program was reviewed, covering the test equipment, the test samples and the testing to be conducted. Of particular note was the discussion in Section 3.2.1 about the neat fuels used directly and as part of blends:
    - Four of the six neat fuels were synthetic
    - Three of the synthetic fuels were renewable sourced
    - Two of the synthetic fuels were out of the normal range expected for cetane testing
- In Section 4.0 the results of the test program were reviewed, leading to the following observations:
    - Despite the fact that the highest and lowest neat samples were in the scope of ASTM D613, current industry practice essentially precludes rating at those levels for routine testing.
    - Even though they were outside the stated scope of method ASTM D6890, the IQT system provided usable data for the high and low samples that ASTM D613 could not run.
    - A review of the precision of the ASTM D6890 results in this program found the data to be in control, even with out of scope samples.
    - The correlation between ASTM D6890 and ASTM D613 is very good (R_{DCN} = 0.9698) considering, once again, that this testing involved fuels outside

the scope of the former method and the blends with a high percentage of highly isomerized paraffins (like ATJ SPK) had a negative effect on cross method reproducibility, Rxy.

- DCN testing is accepted in the specifications that require cetane value testing, and this program substantiates that the data generated is reliable even with synthetic fuels. (High volumes of ATJ SPK have a negative effect on Rxy but as long as the blend amounts are below the recently approved 30% by volume for ASTM D7566-16 Annex A5 ATJ SPK, the cross method reproducibility is acceptable.)
- The ability to make arithmetic approximations of final cetane values using DCN data was confirmed
- ID was shown to be similar in nature to the basic autoignition property, upon which CI is based. It is not used in any specification, at this time (and there are two other methods that gives equivalent DCN values correlated with different ignition delays, a potential source of confusion). Its use will likely remain a research technique.

5.2 CONCLUSION

DCN testing, by ASTM D6890, is satisfactory for evaluating the cetane values for hydrocarbon fuels and fuel blends within current specifications. It can also be used for components out of scope of the device to provide a relative evaluation of ignition quality. That is important for U.S. Army interests in light of the commitment by the U.S. DOD to the use of alternative fuels and fuel components. Since some of these components have cetane values outside of the routine range of traditional CN testing by ASTM D613, this is an important advantage in fuel blending and disposition. Based on this analysis, DCN by ASTM D6890 should become the preferred method for determining the cetane value for the U.S. Army.

5.3 RECOMMENDATIONS

In addition to the conclusion above the following recommendations are offered:

- The relation of chemical structure to cetane value demonstrated in the program suggests that it might be possible to augment or replace the existing Cetane Index methods, which rely solely of the physical chemical properties of the fuel being evaluated. Therefore consideration should be given to using a similar wide range of fuel blends to explore new analytical approaches. While a chemistry adjusted Cetane Index might not be as good as the methods reviewed here, it might be suitable for mobile labs like PQAS-E.
- Using the chemistry adjusted Cetane Index, develop a methodology for using Cetane Improver to improve ignition quality of fuel in the storage. This might be necessary for advanced systems using JP-8, or F-24 in CONUS, which is now, and for the foreseeable future, produced without regard to cetane value.
- Contact the manufacturers and/or distributors of the equipment used in ASTM D7170 and ASTM D7668 to determine if they would conduct tests and provide data for the same eighteen (18) samples. These methods are scoped for a range of samples similar to the scope of ASTM D6890, thus not including the complete range of materials tested in this program. If these methods can provide equivalent data, then it would be simpler to just specify DCN testing in general, regardless of the method.

6.0 REFERENCES

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3. “Distillate Fuel Trends: International Supply Variations And Alternate Fuel Properties”, Interim Report. TFLRF No. 435, G Wilson and S Westbrook, Defense Technical Information Center, 2013
4. ASTM D613, the Standard Test Method for Cetane Number of Diesel Fuel Oil
5. ASTM D6890, the Standard Test Method for Determination of Ignition Delay and Derived Cetane Number (DCN) of Diesel Fuel Oils by Combustion in a Constant Volume Chamber
6. MIL-DTL-83133H A2 Detail Specification, Turbine Fuel, Aviation, Kerosene Type, JP-8 (NATO F-34), NATO F-35, and JP-8+100 (NATO F-37)
7. ASTM D975 the Standard Specification for Diesel Fuel Oils
8. ASTM D7566 the Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons
9. Another type of Annex A2 FT SPK, made by Sasol in South Africa, is synthesized from C2 and C3 olefins which makes a highly isomerized material with a very low cetane value and would likely produce results similar to ATJ SPK
10. Information from Robert Legg, SwRI, who is the chairman of ASTM Subcommittee D02.01 on Combustion Characteristics, the group in charge of D613
11. Since there was only one D613 CN test conducted on each sample, there is no way to evaluate its precision
12. ASTM E177 the Standard Practice for Use of the Terms Precision and Bias in ASTM Test Methods
13. ASTM D6708 the Standard Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material
14. “Alcohol-To-Jet (ATJ) Fuel Blending Study”, Interim Report TFLRF No. 472, S. Hutzler, Defense Technical Information Center, 2013
15. ASTM D7170 the Standard Test Method for Determination of Derived Cetane Number (DCN) of Diesel Fuel Oils—Fixed Range Injection Period, Constant Volume Combustion Chamber Method
16. ASTM D7668 the Standard Test Method for Determination of Derived Cetane Number (DCN) of Diesel Fuel Oils—Ignition Delay and Combustion Delay Using a Constant Volume Combustion Chamber Method